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XVII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

ON THE CUPRIAMMONIUM DOUBLE SALTS.

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Presented May 10, 1893.

IN the course of an extended investigation upon the ammoniacal compounds of copper, undertaken with the hope of obtaining more light upon the vexed question of their structure, a new class of interesting compounds was discovered. The preliminary notice of these compounds was published about a year ago;* but since that time several new ones have been added to the list. It is the object of this paper more fully to describe all of these substances, so far as they have been studied.

The generic feature of the new class is the fact that two different acids — a halogen and an organic acid radical — are united at the same time to the ordinary cupriammonium group. Below are tabulated the formulæ of the compounds, the preparation, properties, and analyses of which are described in the work which follows:—

- (1.) $\text{Cu}(\text{NH}_3)_2\text{BrC}_2\text{H}_3\text{O}_2$.
- (2.) $\text{Cu}(\text{NH}_3)_3\text{ClC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$.
- (3.) $[\text{Cu}(\text{NH}_3)_2\text{ClC}_2\text{H}_3\text{O}_2]_2 \cdot 3 \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 + 7 \text{H}_2\text{O}$.
- (4.) $\text{Cu}(\text{NH}_3)_2\text{BrCHO}_2$.

Besides these compounds two others, which appeared as by-products of the investigation, are worthy of description:—

- (5.) $\text{CuCl}_2 \cdot 2 \text{NH}_4\text{C}_2\text{H}_3\text{O}_2$.
- (6.) $3 \text{CuBr}_2 \cdot 10 \text{NH}_3$.

* Theodore W. Richards, *Berichte der deutsch. chem. Gesellsch.*, 1892, p. 1492. Since the publication of this paper, F. Foerste has announced the discovery of cupriammonium acetate (*Ber. d. ch. Ges.*, 1892, XXV. 3416).

1. *Cupriammonium Acetobromide*,
 $\text{Cu}(\text{NH}_3)_2\text{BrC}_2\text{H}_3\text{O}_2$.

This compound is formed with great ease whenever cupric bromide is treated with alcohol and saturated ammonia water, and the mixture is nearly neutralized with strong acetic acid. For example, five grams of cupric bromide were shaken with ten cubic centimeters of alcohol and the like volume of saturated ammonia water, until all of the copper was converted into cupriammonium bromide. The bright blue precipitate was then immediately dissolved in sixty or seventy cubic centimeters additional of alcohol, and sixteen cubic centimeters of strong acetic acid. Upon cooling the solution, and allowing it slowly to evaporate in the air, large brilliant deep-blue crystals, which apparently belong to the monoclinic system, slowly separated.*

The same substance may be obtained in a similar manner from cupric acetate and ammonic bromide, after treating with ammonia and afterwards with acetic acid.

The new compound is only very slightly soluble in pure alcohol, and is decomposed at once by water into impure cupric hydroxide, ammonic acetate and ammonic bromide. The cupric hydroxide contains large amounts of basic cupric bromide and acetate.

The only satisfactory solvent for it seems to be a strong aqueous solution of ammonic acetate and bromide, containing more or less alcohol. By this singular mixture the compound is not decomposed, even at 70° or 80° C. Acids of course at once decompose and dissolve cupriammonium acetobromide, and alkalis upon boiling set free ammonia and precipitate cupric oxide as usual. The crystals are fairly permanent in the air; they are singularly brittle and rather light, possessing a specific gravity of 2.134.

In the analysis of the compound, copper was determined electrolytically after evaporation with sulphuric and nitric acids; and the bromine and ammonia were determined as usual. The accurate determination of the acetic acid was a much harder task. Distillation with phosphoric acid, according to the method recommended by Fresenius,† is not very satisfactory because of the great expenditure of time which it requires, and the fact that traces of hydrobromic and phosphoric acids are always found in the distillate. Usually the two acids were precipitated together from the neutralized distillate, and the

* T. W. Richards, Ber. d. ch. Ges., 1890, p. 3791.

† Zeit. für Analytische Chem., V. 315, and XIV. 172.

result was calculated as argentic bromide; but in some cases they were determined separately. The presence of phosphoric acid in the distillate is especially unfortunate, because of the uncertainty which it introduces in the end point of the alkalimetric reaction.

On the other hand, quantitative combustion after the usual method, and calculation of the acetic acid from the carbon dioxide formed, is not easy because of the presence of the large amount of bromine.

Analyses of $\text{Cu}(\text{NH}_3)_2\text{BrC}_2\text{H}_3\text{O}_2$.

- I. 0.0685 gr. of the substance yielded 0.01865 gr. of copper upon electrolysis.
- II. 0.1446 gr. of the substance distilled with caustic potash required 12.16 c.c. of a decinormal acid solution for neutralization.
- III. 0.08485 gr. of the substance yielded 0.06705 gr. of argentic bromide.
- IV. 0.3173 gr. of the substance yielded 0.2518 gr. of argentic bromide.
- V. The distillate from a mixture of phosphoric acid and 0.2311 gr. of the substance required 10.11 c.c. of decinormal alkali for neutralization. Approximately corrected for the alkalimetric equivalent of the argentic phosphate and bromide obtained from the distillate this amount becomes 9.90 c.c.

Many other analyses were made of subsequent preparations, in order to be sure of the identity of the crystals prepared in different ways. It is considered unnecessary to publish these, since they agreed essentially with those given above.

No.	Copper.	Ammonia.	Bromine.	$\text{C}_2\text{H}_3\text{O}_2$.
I.	27.23	14.85	33.63	25.27
II.				
III.				
IV.				
V.			33.78	
Average,	27.23	14.35	33.70	25.27

Average Results.

	Calculated for $\text{Cu}(\text{NH}_3)_3\text{BrC}_2\text{H}_3\text{O}_2$.	Found.
Copper	26.87	27.23
Ammonia	14.42	14.35
Bromine	33.79	33.70
Acetic Acid	24.92	25.27
	<hr/> 100.00	<hr/> 100.35

2. *Ammon-Cupriammonium Acetochloride*,
 $\text{Cu}(\text{NH}_3)_3\text{ClC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$.

Almost any mixture which brings together in concentrated solution copper, chlorine, much acetic acid, and an excess of ammonia yields ammon-cupriammonium acetochloride upon the addition of alcohol. The substance consists of brilliant blue scales, having a pearly lustre. These crystals lose ammonia and water slowly upon exposure to the air, with marked alteration of color; they are decomposed by water, a small amount of the copper going into solution. For analysis the crystals were pressed between filter paper as rapidly as possible. A bromine compound similar in every respect to this one has been prepared, and will form the subject of a future communication.

Analyses of Ammon-Cupriammonium Acetochloride.

- I. 0.2524 gr. of the substance yielded on electrolysis 0.0698 gr. of copper.
- II. 0.2273 gr. of the substance yielded 0.0634 gr. of copper.
- III. 0.2875 gr. of the substance yielded 0.0808 gr. of copper.
- IV. 0.1337 gr. of the substance required on distillation 17.37 c.c. of decinormal acid to neutralize the ammonia volatilized.
- V. 0.1554 gr. of the substance required in the same way 20.17 c.c. of acid.
- VI. 0.0979 gr. of the substance required 12.56 c.c. of decinormal acid.
- VII. 0.2708 gr. of substance yielded 0.1704 gr. of argentic chloride.
- VIII. 0.2696 gr. of substance yielded 0.1700 gr. of argentic chloride.
- IX. 0.1926 gr. of the substance yielded upon distillation with phosphoric acid a distillate requiring 8.94 c.c. of decinormal baric hydroxide for neutralization with phenol phthalein. This liquid yielded 0.0116 gr. of argentic chloride, containing traces of argentic phosphate, which amount is equivalent to about 0.81 c.c. of decinormal acid. Hence the acetic acid in the distillate must have required 8.13 c.c. of the alkaline solution.

X. 0.2215 gr. of substance required upon distillation 10.38 c.c. of baric hydrate, of which 0.66 were required to neutralize the hydrochloric acid corresponding to 0.0096 gr. of argentic chloride obtained from the neutralized distillate ($10.38 - 0.66 = 9.72$).

No.	Copper.	Ammonia.	Chlorine.	C ₂ H ₃ O ₂ .
I.	27.65			
II.	27.89			
III.	28.17			
IV.		22.16		
V.		22.14		
VI.		21.89		
VII.			15.56	
VIII.			15.59	
IX.				24.91
X.				25.90
Average,	27.90	22.06	15.57	25.40

The averaged results are given below.

	Calculated for Cu(NH ₃) ₃ ClC ₂ H ₃ O ₂ · H ₂ O.	Found.
Copper	27.98	27.90
Ammonia	22.53	22.06
Chlorine	15.60	15.57
Acetic Acid	25.97	25.40
Water (by difference)	7.92	9.07
	<u>100.00</u>	<u>100.00</u>

3. *Complex* * *Cupriammonium Acetochloride*,
 $[\text{Cu}(\text{NH}_3)_2\text{ClC}_2\text{H}_3\text{O}_2]_2 \cdot 3 \text{NH}_4\text{C}_2\text{H}_3\text{O}_2 + 7 \text{H}_2\text{O}.$

The complex cupriammonium acetochloride is obtained under conditions which would have been expected to produce the simple compound

* "Complex" is used here in default of a word more capable of describing the complexity of the compound. It is not intended to carry with it any tech-

enclosed in the brackets above. This simple compound, probably owing to its great solubility, we have been unable as yet to isolate. Whenever cupric chloride is treated with a great excess of concentrated ammonia water, the excess cautiously neutralized with glacial acetic acid, and the whole treated with alcohol and allowed to evaporate, great crystals of the complicated compound containing three molecules of ammoniac acetate and probably seven of water to every two of cupriammonium acetochloride always separate out. The addition of somewhat more acetic acid in this case constitutes the sole difference between the methods of preparing this compound and the preceding. In the former case an excess of ammonia was required.

The crystals of the complex salt are of a most brilliant blue with a tinge of violet, and may be obtained of almost any size. They dissolve in very small amounts of water without apparent decomposition, but larger amounts of water decompose them. The new compound readily loses water and ammoniac acetate in the air, and is converted into a pale green powder, which remains to be investigated. Over caustic potash in a desiccator, on the contrary, it is soon converted into a pale violet powder with a very sudden loss of weight. After the sudden decrease has stopped a slower decrease continues, without change of color, and the composition of the powder constantly approaches that of the simple cupriammonium acetochloride. Its complete conversion into this compound we have not yet been able to accomplish; and regarding the exact nature of the compounds which are marked by the irregular decrease in weight we have as yet nothing to say.

For analysis the crystals were pressed between filter paper. The possible causes of error from decomposition on the one hand, and the adhesion of mother liquor on the other, were guarded against as much as possible. Nevertheless these causes of error are undoubtedly responsible for the not unreasonable variations noticeable in the analytical results; for the three specimens of crystals analyzed were undoubtedly identical.

Analyses of Complex Cupriammonium Acetochloride.

- I. 0.2404 gr. of the substance yielded on electrolysis 0.0411 gr. of copper. .
- II. 0.2446 gr. of the substance yielded on electrolysis 0.0419 gr. of copper.

nical meaning with regard to the structure of the molecule. Indeed, the names of all the compounds described in this paper are far from satisfactory to us; they would be thrown out very gladly if better ones could be found.

- III. 0.2772 gr. of the substance yielded on electrolysis 0.0476 gr. of copper.
- IV. 0.1418 gr. of the substance yielded on distillation enough ammonia to neutralize 13.25 c.c. of decinormal acid.
- V. 0.1403 gr. of the substance required on distillation 13.24 c.c. of decinormal acid.
- VI. 0.1895 gr. of the substance required on distillation 17.79 c.c. of decinormal acid.
- VII. 0.1472 gr. of the substance required on distillation 14.19 c.c. of decinormal acid.
- VIII. 0.2319 gr. of the substance yielded 0.0895 gr. of argentic chloride.
- IX. 0.2244 gr. of the substance yielded 0.0870 gr. of argentic chloride.
- X. 0.1679 gr. of the substance gave on combustion 0.0998 gr. of carbon dioxide.

No.	Copper.	Ammonia.	Chlorine.	$C_2H_5O_2$.
I.	17.10			
II.	17.13			
III.	17.17			
IV.		15.95		
V.		16.11		
VI.		16.03		
VII.		16.46		
VIII.			9.54	
IX.			9.59	
X.				39.95
Average	17.13	16.16	9.57	39.95

A fourth sample, which had a similar appearance, was found to contain 17.61 per cent of copper and 9.94 of chlorine. This had probably begun to lose water and ammoniac acetate. A finely powdered specimen kept for eleven months over sodic hydrate was found to con-

tain 25.8 per cent of copper and 14.35 of chlorine. Since the theoretical percentages corresponding to $\text{Cu}(\text{NH})_2\text{ClC}_2\text{H}_3\text{O}_2$ are respectively 33.08 and 18.45, it is clear that the excess of ammoniac acetate had not been wholly decomposed during the long exposure. Further experiments in this direction will be made in the near future.

Results.

	Calculated for $\text{Cu}_2(\text{NH}_3)_4\text{Cl}_2(\text{C}_2\text{H}_3\text{O}_2)_5(\text{NH}_4)_3\cdot 7\text{H}_2\text{O}$.	Found.
Copper	17.12	17.13
Chlorine	9.55	9.57
Ammonia	16.08	16.16
$\text{C}_2\text{H}_3\text{O}_2$	39.73	39.95

4. *Cupriammonium Formibromide*, $\text{Cu}(\text{NH}_3)_2\text{BrCHO}_2$.

Cupriammonium formibromide is made after a method essentially similar to that employed in making the corresponding compound of acetic acid. The salt is more difficult to obtain in a pure state; but any reasonably concentrated solution containing bromine, copper, much formic acid, and ammonia in very slight excess, will deposit the deep "robin's egg" blue crystals of the desired salt upon the addition of alcohol. The possibility of the formation of basic salts of copper is diminished if the excess of ammonia is added after the addition of the alcohol. The salt possesses no unexpected properties, except that the color of the short needles is much less brilliant and crude than that of cupriammonium acetobromide.

A similar compound containing chlorine instead of bromine has been prepared, and analyzed with results which were sufficiently accurate to show the identity of the compound; but it was thought desirable to study more carefully the conditions necessary for its preparation in a pure state before publishing the results. Moreover, a more complex formibromide of most interesting aspect and composition has been made. This substance also awaits further study.

Analyses of Cupriammonium Formibromide.

- I. 0.2192 gr. of the substance gave on electrolysis 0.0621 gr. of copper.
- II. 0.2164 gr. of the substance yielded on electrolysis 0.0618 gr. of copper.

- III. 0.1386 gr. of the substance yielded a distillate of ammonia which required for neutralization 12.32 c.c. of decinormal acid.
- IV. Similarly 0.1180 gr. of the substance required 10.46 c.c. of decinormal acid.
- V. 0.1599 gr. of the substance gave 0.1371 gr. of argentic bromide.
- VI. 0.2414 gr. of the substance gave 0.2063 gr. of argentic bromide.
- VII. 0.1678 gr. of the substance gave 0.1429 gr. of argentic bromide.
- VIII. 0.2062 gr. of the substance yielded on combustion 0.0403 gr. of carbon dioxide.
- IX. 0.2435 gr. of the substance yielded on combustion 0.0469 gr. of carbon dioxide.

No.	Copper.	Ammonia.	Bromine	Formic Acid, CHO ₂ .
I.	28.30			
II.	28.56			
III.		15.17		
IV.		15.13		
V.			36.49	
VI.			36.37	
VII.			36.24	
VIII.				19.93
IX.				19.70
Average,	28.43	15.15	36.37	19.80

These analyses were made from several different samples (especially V., VI., and VII., which were all different), and hence they prove the definiteness of the compound. The averaged results are given below.

	Calculated for Cu(NH ₃) ₂ BrCHO ₂ .	Found.
Copper	28.56	28.43
Ammonia	15.33	15.15
Bromine	35.90	36.37
CHO ₂	20.21	19.80
	100.00	99.75

5. *Cupric Ammonic Acetochloride*,
 $\text{CuCl}_2 \cdot 2 \text{NH}_4\text{C}_2\text{H}_3\text{O}_2$.

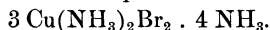
Upon several occasions during the investigation just described, when concentrated solutions of approximately equivalent amounts of cupric chloride and ammoniac acetate had been allowed to evaporate together, especially with addition of alcohol, bright green almost cubical crystals separated. These crystals were sometimes found to be mixed with small amounts of ammoniac chloride, and sometimes almost pure. The substance is a double salt, and not a cupriammonium compound; hence it dissolves in water without apparent decomposition. The purest crystals gave the following analytical results.

Analyses of Cupric Ammonic Acetochloride.

- I. 0.3132 gr. of the substance gave 0.0689 gr. of copper.
- II. 0.2649 gr. of the substance gave 0.0585 gr. of copper.
- III. 0.1180 gr. of the substance gave 0.1181 gr. of argentic chloride.
- IV. 0.2091 gr. of the substance gave 0.2150 gr. of argentic chloride.
- V. 0.2121 gr. of the substance yielded enough ammonia to require 14.47 c.c. of decinormal acid.
- VI. 0.2158 gr. of the substance required 14.20 c.c. of acid.
- VII. 0.1930 gr. of the substance required 13.83 c.c. of acid.
- VIII. 0.2648 gr. of the substance gave 0.1633 gr. of carbon dioxide.

No.	Copper.	Chlorine.	Ammonium.	$\text{C}_2\text{H}_3\text{O}_2$.
I.	22.00			
II.	22.09			
III.		24.75		
IV.		25.35		
V.			12.34	
VI.			11.88 (?)	
VII.			12.98	
VIII.				41.35
Average,	22.05	25.05	12.40	41.35

	Calculated for $\text{Cu}(\text{NH}_4)_2\text{Cl}_2 \cdot \text{C}_2\text{H}_3\text{O}_2 \cdot 2$.	Found.
Copper	22.03	22.05
Chlorine	24.56	25.05
Ammonium	12.52	12.40
Acetic Acid	40.89	41.35
	<u>100.00</u>	<u>100.85</u>

6. *Tetrammon-Tricupriammonium Bromide,*

Long ago Rammelsberg* described two compounds of ammonia and cupric bromide, to one of which, consisting of dark green crystals, he ascribed the formula $\text{CuBr}_2 \cdot 3 \text{ NH}_3$; and to the other, consisting of a bright blue powder, he ascribed the formula $\text{CuBr}_2 \cdot 5 \text{ NH}_3$. Recent investigation† has shown that the latter of the two substances must have been in reality $\text{CuBr}_2 \cdot 6 \text{ NH}_3$, which had lost some of its very loosely combined ammonia by exposure to the air. The same investigation brought to light an olive-green substance having the formula $\text{Cu}(\text{NH}_3)_2\text{Br}_2$.

Repeated attempts were made at the same time to obtain Rammelsberg's first substance. The product of these trials invariably consisted of deep indigo, almost black crystals, which contained noticeably more ammonia than the amount required by Rammelsberg's formula. These deep blue crystals are best obtained by adding very cautiously strong hydrobromic acid to a mixture of cupric bromide, alcohol, and just enough aqua ammonia to keep all the copper in solution. Upon the addition of enough acid to neutralize the ammonia, the crystals — which are almost insoluble in alcohol — begin to form.

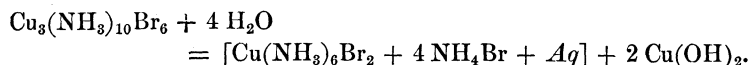
Upon exposure to the air in a moist state these crystals lose ammonia rather rapidly; but when dry they are much more stable. Gentle heat (160°) readily converts them completely into the olive-green $\text{Cu}(\text{NH}_3)_2\text{Br}_2$, which still retains the crystalline form of the more complex salt. It is not impossible that Rammelsberg's green crystals consisted originally of the indigo-colored substance, which had lost superficially a little of its ammonia.

Tetrammon-tricupriammonium bromide is decomposed by water, a noticeable amount of copper going into solution in the form of a sol-

* Pogg. Annalen, LV. 246.

† T. W. Richards, Ber. d. ch. Ges., 1890, p. 3790.

uble compound containing proportionally more ammonia than the original substance. The reaction which takes place may possibly be represented somewhat as follows:—



The amount of water present undoubtedly determines to a large extent the exact nature of the cupriammonium compound which remains undecomposed.

A great number of analyses of the indigo salt were made; partly because of the unusual nature of the formula which they indicated; and partly because the crystals, constantly appearing under many varying conditions in the work which has just been described, needed identification.

Analyses of $\text{Cu}_3(\text{NH}_3)_{10}\text{Br}_6$.

- I. 0.4730 gr. of the substance yielded 0.1075 gr. of copper.
- II. 0.4540 gr. of the substance yielded 0.1033 gr. of copper.
- III. 0.2614 gr. of the substance yielded 0.0594 gr. of copper.
- IV. 0.4269 gr. of the substance yielded 0.5721 gr. of argentic bromide.
- V. 0.4084 gr. of the substance yielded 0.5476 gr. of argentic bromide.
- VI. 0.2884 gr. of the substance yielded 0.3861 gr. of argentic bromide.
- VII. 0.1776 gr. of the substance yielded an amount of ammonia requiring 20.67 c.c. of decinormal acid for neutralization.
- VIII. 0.1245 gr. of the substance required 14.77 c.c. of the same acid.
- IX. 0.1099 gr. of the substance required 12.71 c.c. of the same acid.
- X. 0.1288 gr. of the substance required 15.20 c.c. of the same acid.
- XI. 0.1175 gr. of the substance required 13.85 c.c. of the same acid.

No.	Copper.	Bromine.	Ammonia.
I.	22.73		
II.	22.75		
III.	22.72		
IV.		57.03	
V.		57.06	
VI.		56.97	
VII.			19.86
VIII.			20.25
IX.			19.74
X.			20.14
XI.			20.19
Average,	22.73	57.02	20.06

Result.

	Calculated for $\text{CuBr}_2\cdot 3\text{NH}_3$.	Calculated for $(\text{CuBr}_2)_2(\text{NH}_3)_{10}$.	Found.
Copper	23.15	22.68	22.73
Bromine	58.21	57.03	57.02
Ammonia	18.64	20.29	20.06
	100.00	100.00	99.81

It is evident that this paper is merely an introduction to the possibilities in the direction indicated. Not only have other compounds of the same acids been already discovered, but many other acids, notably hydriodic, lactic, sulphocyanic, etc., show that they are capable of forming similar compounds. Moreover, the substituted ammonias may apparently take the place of the simple substance in most of the compounds. A few of these preparations are to be seen in the University exhibit at the World's Columbian Exhibition. The study of all these interesting substances will be continued in the immediate future at this Laboratory.